

IR SPECTRA OF OXYGEN ADSORBED ON SnO_2

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IR spectra of oxygen adsorbed on SnO_2 with and without lattice defects have been studied. At low temperatures oxygen is adsorbed on defect SnO_2 in two forms of O_2^- . This supports the earlier results obtained by ESR. The low-temperature forms of adsorbed oxygen (unrevealed in ESR spectra) were detected on defectless SnO_2 . High-temperature forms of adsorbed oxygen appear in the IR-spectra as bands due to vibrations of the cation-oxygen bond.

Изучены ИК-спектры кислорода адсорбированного на дефектной и недефектной SnO_2 . Показано, что на дефектной двуокиси олова кислород при низких температурах адсорбируется в виде двух типов O_2^- , что подтверждает результаты полученные ранее методом ЭПР. На недефектной SnO_2 обнаружено образование низкотемпературной формы адсорбции кислорода не проявляющейся в спектрах ЭПР.

To elucidate the mechanisms of catalytic reactions, information is needed about the forms of oxygen stabilization at the catalyst surface during adsorption. By using IR spectroscopy, a distinction of the molecular /1, 2/ and atomic /2-5/ forms of adsorbed oxygen is possible.

In the present paper the reactions of oxygen with the surface of SnO_2 (I) and SnO_2 (II) were studied by IR spectroscopy.

Precipitation from the solution of stannic chloride with ammonia followed by drying at 100°C was used to obtain samples of tin dioxide. After drying, the samples were treated at 450°C in vacuum for 2 hrs and then cooled to room temperature to retain an irregular structure. These samples will be referred to as irregular (SnO₂(I)). Normal tin dioxide (SnO₂(II)) was obtained by calcining dried samples in air at 450-500°C. The specific surface area of the samples was determined by measuring the low-temperature adsorption of argon and calculated by the BET technique. It was equal to 47-50 m²/g for SnO₂(I) and 20 m²/g for SnO₂(II).

For the experiments, the samples were pressed into 3.5 x 1.5 cm pellets at a pressure of 8-10 t/cm². The sample thickness was 20-30 mg/cm². IR spectra were recorded using a modified UR-10 spectrometer which allowed measurements at high temperatures /6/ in a cuvette with a flange packing. The cuvette was separated from the vacuum compartment by a metal stopcock to avoid surface contamination with grease vapours.

The spectra were recorded in the range of 700-3900 cm⁻¹ using LiF and NaCl prisms. The slit width was 8 cm⁻¹ at 1000 cm⁻¹. In the initial IR spectra of SnO₂(I) (as opposed to SnO₂(II)) two absorption bands were observed at 1340 and 1570 cm⁻¹.

The change in the duration of treatment under oxygen or vacuum from 1 hr to 10 hrs affects insignificantly the spectrum in the region 1300-1600 cm⁻¹.^{*} These bands can be ascribed to the structures originating in the bulk due to the presence of the admixed carbon and nitrogen atoms^{**}. Oxygen adsorption on such a sample at

^{*}It is noteworthy that unlike a normal sample of SnO₂ (see below), a defect sample affects only insignificantly the total transmission of the sample during this treatment.

^{**}The correct assignment of the maxima observed to the admixture vibrations is supported by the absence of these bands in the spectrum of a normal sample.

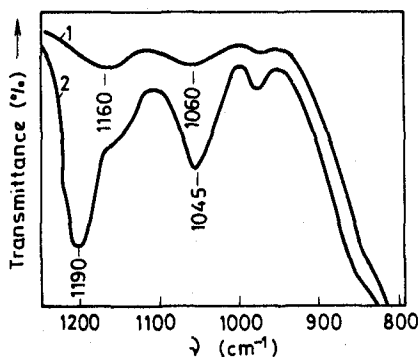


Fig. 1. Variation of the IR spectra of defect tin dioxide during oxygen adsorption. 1 -- initial spectrum of SnO₂(I); 2 -- oxygen adsorption ($P_{O_2} = 50$ Torr, $t = 20^\circ\text{C}$)

20°C (-70°C) results in the appearance of two intensive absorption bands at 1190 and 1045 cm^{-1} (Fig. 1, curve 2). In addition, an absorption shoulder at 1060 cm^{-1} in the 1190 cm^{-1} band and a weak absorption band at 970 cm^{-1} are observed. At the same time bands within the $1300\text{-}1600\text{ cm}^{-1}$ range do not vary. Heating the sample over 300°C either in vacuum or in oxygen results in the disappearance of the bands at 1190 and 1045 cm^{-1} . The first maximum disappears during desorption at temperatures below 200°C , while the second one is not observed at temperatures higher than 300°C .

A study of the ESR spectra of oxygen adsorbed on SnO₂(I) shows that two types of ion-radicals O_2^- are formed which are stabilized on Sn^{4+} and $\text{Sn}^{2+}/7/$. Similarly to the IR spectra of oxygen adsorbed on TiO₂ at $20^\circ\text{C}/2/$, the intensive bands at 1190 and 1045 cm^{-1} can be ascribed to the vibrations of the O—O bond in the ion-radical forms of adsorbed oxygen of type O_2^- . One can suggest that the 1190 cm^{-1} band in the IR spectra corresponds to the vibrations of the O—O bond in the ion-rad-

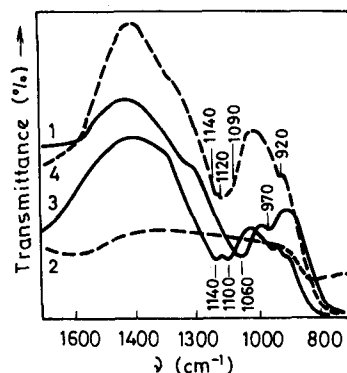


Fig. 2. IR spectra of SnO₂(II). 1 — initial spectrum in vacuum; 2 — treatment under vacuum ($t = 400^{\circ}\text{C}$, $\tau = 2$ hrs); 3 — oxygen adsorption ($P_{\text{O}_2} = 50$ Torr, $t = 20^{\circ}\text{C}$); 4 — in O₂ after 1 hour

ical O₂⁻ stabilized on Sn⁴⁺ while the 1045 cm⁻¹ band to the vibrations of the O-O bond in the ion-radical O₂⁻ stabilized on Sn²⁺. An ion-radical stabilized on Sn⁴⁺ is thermally less stable and decomposes below 200°C. At the same time, ion-radicals stabilized on Sn²⁺ are rather stable up to 300°C. This is in good agreement with the results obtained by an ESR study /7/.

Figure 2 (curve 1) gives the spectrum of normal tin dioxide (SnO₂(II)) calcined in air. Two absorption bands were observed at 1060 and 970 cm⁻¹. As the sample is treated in vacuum (curve 2) at 400°C for 2 hrs, the transmission slowly decreases. As a result of a subsequent increase of the heating time at 400°C, the sample becomes opaque. Cooling of the sample down to room temperature in vacuum does not lead to the reduction of its transmission. Such a behaviour is usually ascribed to the presence of electrons which absorb in the conductivity zone /2, 8, 9/. During reduction, Sn⁴⁺ ions are partially converted into the trivalent state, as supported by the ESR spectra /7/. An oxygen loss takes place and free electrons appear in the conductivity

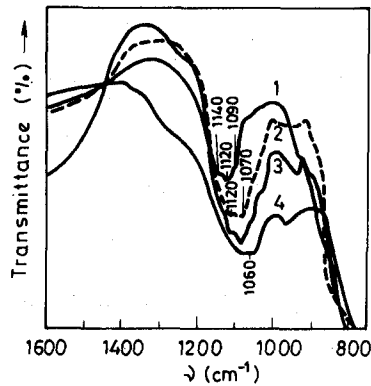


Fig. 3. IR spectra of oxygen adsorbed on SnO_2 (II). 1 - 20°C ; 2 - 100°C ; 3 - 200°C ; 4 - 400°C

zone, which leads to a significant increase in the background absorption. As is seen in Fig. 1, curve 3, the sample transmission is completely reduced already at room temperature as oxygen is admitted and then it increases with the time of exposure to oxygen (curve 4). This is a natural effect since oxygen is an electron trap. It is noteworthy that the reaction with oxygen at 20°C does not lead to the disappearance of absorption in the region above 1500 cm^{-1} , which may also be due to the presence of free carriers /2/ and which disappears only after the heating of the sample in oxygen at 400°C . Reaction with oxygen at 20°C results in the appearance of a series of absorption bands in the $800\text{--}1200\text{ cm}^{-1}$ region. The most intensive band has a center at 1100 cm^{-1} and two bands in the low-frequency region (curve 4). As the temperature is increased to 100°C , the high-frequency shoulder at 1140 cm^{-1} of the 1100 cm^{-1} band disappears, and the broadening of this band toward low frequencies occurs (Fig. 3, curve 2). Further increase in temperature to 400°C leads to the increase in absorption in the 1060 cm^{-1} region and to the increase in absorption in the 1060 cm^{-1} region and to the disappearance of the high-frequency shoulders. At

400°C a band with a maximum at 1060 cm^{-1} and a band at 960 cm^{-1} can be observed. Apparently these bands (the same maxima were observed on SnO_2 (I)) can be ascribed to the high-temperature products of the reaction of oxygen with tin dioxide. These bands may characterize the stretching of several different bonds: surface cation-oxygen of type Sn-O and Sn=O /10/. The assignment of these absorption bands to the vibrations of Me-O bonds is confirmed by their diminishing in CO due to the formation of carbonate complexes.

The high-frequency maxima at 1100, 1140, 1120 and 1090 cm^{-1} , which disappear below 200°C, can be assigned to the stretching vibrations in the low-temperature forms of adsorbed oxygen. They can be, e. g., ion-radical forms from adsorbed oxygen of the type O_2^- whose O-O stretching band is in satisfactory agreement with the band position observed for TiO_2 /2/ and defect SnO_2 . However, the ESR spectra of oxygen adsorbed on such a sample did not indicate the appearance of the ion-radical forms /7/. Thus, the bands observed in this work can be ascribed to the vibrations of the O-O bond which, in order of magnitude, are close to the stretching vibrations in the ion-radical form. This form is not revealed by the ESR spectra owing to reasons such as the stabilization of O_2^- at a paramagnetic center of the type Sn^{3+} which is likely because the frequency (1100 cm^{-1}) is between the values for the O_2^- ion stabilized on Sn^{4+} (1190 cm^{-1}) and on Sn^{2+} (1045 cm^{-1}), as has been shown for O_2^- adsorption on defect SnO_2 . Another possibility for assigning the maxima connected with the low-temperature forms of oxygen adsorption can be the formation of complexes with more than two atoms of oxygen $[\text{O}_3]$ and $[\text{O}_4]$, on the surface. As the literature data show /11-14/, the position of bands observed by us corresponds to uncharged complexes $[\text{O}_3]$ /11/ or $[\text{O}_4]$ /13/. The absorption bands of the charged complexes $[\text{O}_3^-]$, $[\text{O}_4^-]$ are in the lower frequency range (1000 cm^{-1}).

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The study of the IR spectra of oxygen containing ¹⁸O isotope a mixture of ¹⁶O₂ and ¹⁸O₂ was adsorbed) did not permit to distinguish the forms of adsorbed oxygen since absorption of split bands coincided with the self-absorption of the adsorbent and with the bands of adsorbed oxygen ¹⁶O.

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